

Received by OSTI

NOV 16 1990

SAND--90-1828C

DE91 002697

SAND90-1828A C
Unlimited Release
Printed October 1990

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ON
POLY-3-METHYLTHIOPHENE

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IN-SITU DERIVATIVE CYCLIC VOLTABSORPTOMETRIC STUDIES
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ABSTRACT

Spectroscopic behavior of poly-3-methylthiophene (P3MT) has been studied employing derivative cyclic volt-absorptometric (DCVA) techniques. In the DCVA technique, the derivative absorption signal (da/dt) is recorded as a function of the applied potential. The da/dt signals, the spectroscopic analog of electrochemical currents in cyclic voltammetry, are capable of monitoring the potential dependency for the absorption band effectively discriminating against nonfaradaic signals. The DCVA studies on the P3MT system show that the neutral form of P3MT, absorbing at 490 nm (at less than 0.3 V vs. Ag), changes to the radical cation form, which absorbs at 760 nm. Initially, the formation of the radical cation goes through an isosbestic point, indicating that the conversion of the neutral to radical (polaron) form is chemically reversible. However, upon increasing the electrode potential, the rate of the radical formation at 760 nm starts to decrease, with the formation of another band at about 1250 nm, attributable to a quinoid (bipolaron) form. This trend begins above about 0.6 V, shifting to a more positive voltage as the thickness of the film grows. This observation indicates that the electrochemical conversion of the neutral to radical form, followed by the quinoid form, is a slow process controlled by the diffusion of counter ions through the film. *In-situ* conductivity measurements as a function of applied potentials and chronoamperometric results support the observed spectroscopic behavior.

INTRODUCTION

Interest in conducting polymers was stimulated by Little's suggestion of superconductivity in organic materials in the mid-1960's [1a]. Since Shirakawa, MacDiarmid and coworkers demonstrated the semiconducting and metallic properties of polyacetylene, a linear conjugated organic polymer, in 1977 [1b], a surge of interest in this class of materials has been shown in the literature resulting in a number of review articles, books, and symposium volumes [2-8]. Of the many different types of organic conducting polymers, polythiophene and its substituted analogs appear to offer greater environmental stability with a more rigid, yet similar, structure to polyacetylene. The higher stability may accrue from the large electronic shell of the sulfur atom, making the free carrier available more readily at lower chemical potentials.

Preparations of polythiophenes with various substituted monomer units have been reported, and their physical/chemical properties have been evaluated [9-14]. UV-vis [15a, 15b] and infrared absorption spectra [10a, 10b], as well as morphological studies [9, 10a] of electrochemically prepared polythiophenes have recently been reported. These studies show that the conducting polymer has a porous network structure. The oxidized form is conductive, whereas the reduced

form is semiconducting. In this study, we use a combination of cyclic voltammetry and spectrometric measurements to study the doping behavior of poly-3-methylthiophene, a substituted polythiophene.

EXPERIMENTAL

Experiments were carried out in propylene carbonate (PC, reagent grade) with lithium perchlorate (reagent grade) as the supporting electrolyte. The 3-methylthiophene monomer obtained from Aldrich (99+%) was used as received. The polymer films were grown on working electrodes, gold or platinum, with a silver wire pseudo-reference electrode in a solution containing 0.50 M supporting electrolyte and approximately 1.0 M monomer. Electro-polymerization was done galvanostatically at $175 \mu\text{A}/\text{cm}^2$ with a platinum electrode, or by potentiostatically scanning between 0.0 and 1.8 volts with the gold interdigitated grid electrode (Fig. 1.) in PC/LiClO₄ [16]. Scan rates were typically 50 mV/sec, unless specified otherwise.

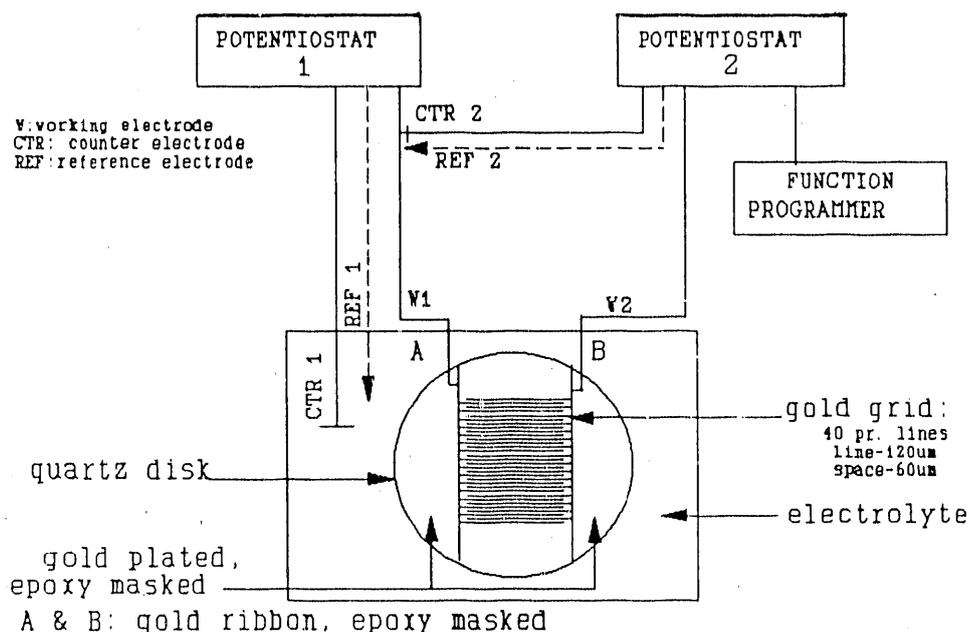


Fig. 1. Drawing of the electrode and cell configuration for conductivity experiments.

The near normal incidence reflectance spectroelectrochemistry (NNIRS) setup has been described elsewhere [17]. A Princeton Applied Research (PAR) Model 173 potentiostat and PAR 175 function generator were used to control potentials at the working electrode. The cell consisted of a platinum working electrode, which was polished to a mirror finish with $1 \mu\text{m}$ METADI[®] polishing compound from Buehler Ltd., a silver wire pseudo-reference electrode, and a spiral platinum counter electrode. Data acquisition and stepper motor control to drive the monochromator were accomplished by using an IBM-XT computer with a Keithley 570 interface board. A film of $0.04\text{-}\mu\text{m}$ thickness was grown galvanostatically at $40 \mu\text{A}$ on a 0.23-cm^2 platinum electrode.

For the conductivity studies, films of $1 \mu\text{m}$ and $5 \mu\text{m}$ were grown on a quartz electrode with interdigitated $120\text{-}\mu\text{m}$ gold lines and $60 \mu\text{m}$ spacing as shown in Fig. 1 by potentiostatically scanning from 0 to 1.8 volts and holding at 1.7 V vs. silver until the desirable thickness was obtained. The interdigitated

electrode was fabricated by electroplating in a Dequest 2000 gold cyanide bath on a quartz disk, one inch in diameter and 1/16 inch thick. Leads A and B in Fig. 1 were connected together as the working electrode during film growth. Films were studied in three concentrations of LiClO_4 in PC (0.5, 0.05 and 0.005 M.) Conductivity measurements were made by holding the film at a given potential with one potentiostat, and recording the current-potential (I-V) curves with a second potentiostat by scanning from 0 to 110 mV vs. Ag at 10 mV/s.

RESULTS AND DISCUSSION

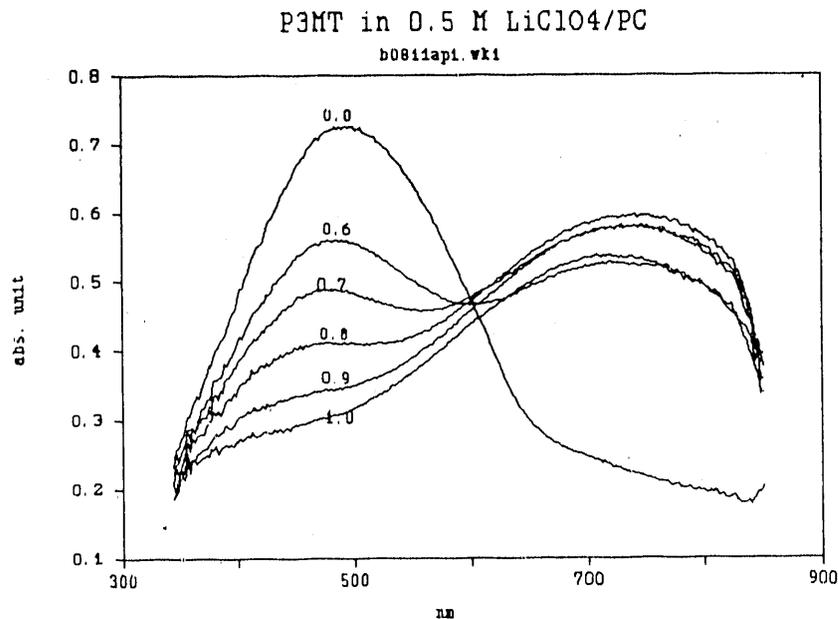


Fig. 2. Visible spectra of P3MT obtained with NNIRS.

Fig. 2 shows a family of visible spectra of a P3MT film in 0.5 M LiClO_4/PC as a function of applied potential. Spectra are taken after equilibrium has been reached at a given potential. The absorption maximum observed at about 480 nm is attributed to the $\pi - \pi^*$ transition of the basic thiophene aromatic structure. The broad band at 750 nm is due to the polaron absorption in the oxidized polymer. Isosbestic points are observed at about 640 nm. An isosbestic point indicates a fixed stoichiometric relationship between the two states, and supports the high chemical reversibility of the doping process. This reversible doping-undoping is a unique characteristics of polyene (polymer with conjugated π bond) conducting polymers. An isosbestic point is obtained between 0.0 and 0.6 V. Another isosbestic point is obtained between 0.7 and 0.8 V. At above 0.8 V, absorbance of the film is reduced; this indicates film degradation (as shown at 0.9 and 1.0 V). These behavior indicates a total of two process occurs sequentially before the film degrades. The spectra of the same film in 0.05 M and 0.005 M of LiClO_4 are essentially the same (Spectra not shown).

The cyclic voltammograms (CV's) of a 0.04- μm P3MT film in Fig. 3 show changes as a function of the LiClO_4 concentrations. The anodic peaks are not visible; however, CVs with less noise have been obtained with thicker films [15a]. The CV signal increases, as well as the noise level decreases, as the LiClO_4 concentration decreases. The DCVA data is a plot of derivative absorbance (dA/dt) signal as a function of the scanning potential [18-19]. Here A represents absorbance signal recorded at a given wavelength and t is time. The DCVA plots show the voltammetric behavior of a species absorbing photons at a given wavelength. This eliminates the interference signals originating from both nonfaradaic and some faradaic processes. Signals from the faradaic (redox)

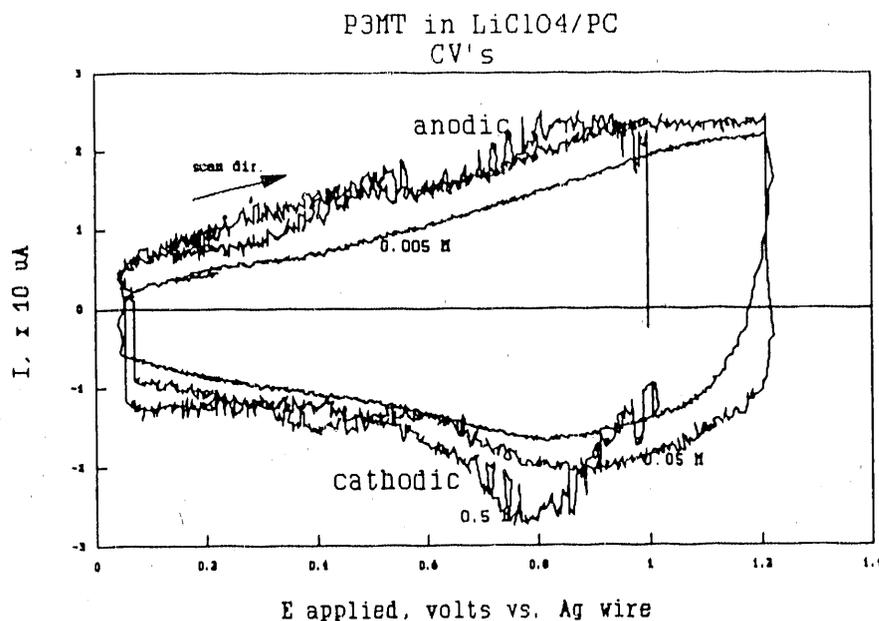


Fig. 3. CV's of P3MT in 0.5 M, 0.05 and 0.005 LiClO₄/PC.

processes for a species which does not absorb photons at this wavelength are eliminated.

Figs. 4 & 5 show the DCVA plots at 750 and 482 nm respectively. The effect of concentration of LiClO₄ is obvious in Fig. 4 at 750 nm. The first oxidized species starts to form as the potential is scanned to the anodic region, showing its peak maximum at 0.2 V in 0.5 M LiClO₄ and at 0.4 V in 0.05 M, then at 0.6 V in 0.005 M. Similarly, the point where the first oxidized species shows depletion, where dA/dt equals to zero, also shifts to a more positive potential as the concentration of the supporting electrolyte decreases. Perhaps this is caused by the additional overpotential required to oxidize the film as the conductivity of the supporting electrolyte decreases. The positive shift in CV

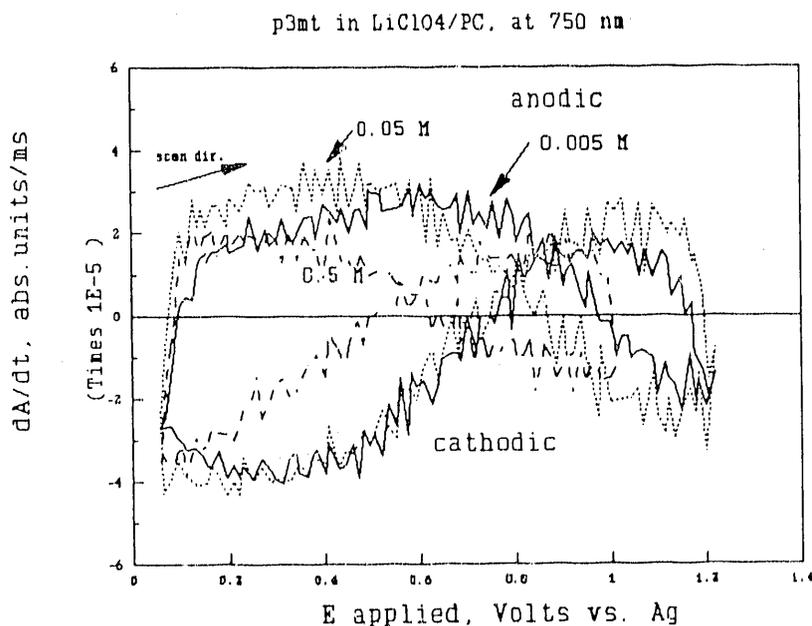


Fig. 4. DCVA of P3MT in 0.5 M, 0.05 M and 0.005 M LiClO₄/PC at 750 nm.

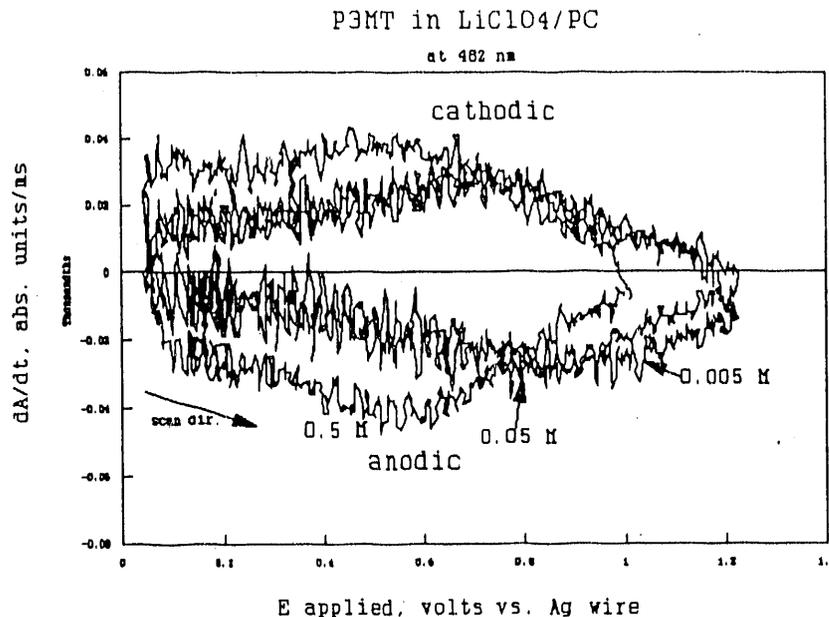


Fig. 5. DCVA of P3MT in 0.5 M, 0.05 and 0.005 M LiClO₄/PC at 482 nm.

peak potentials is also observed as a function of film thickness [20]. As the thickness increases, the time of diffusion of counter ions through the thickness increases as well. This phenomenon indicates that the redox reaction in the film occurs under diffusion control of the counter ions.

The DCVA curves at 482 nm (Fig. 5) show that the undoped species is depleted as the applied potential becomes more positive. The concentration of the species absorbing at 750 nm (Fig. 4) shows an increase at the expense of this species until the potential gets to 0.2 - 0.6 V, depending on the thickness of the film. At this potential, a more oxidized species absorbing at 1250 nm (the bipolaron) begins to be generated at the expense of the first oxidized species [15]. This indicates that more than one processes occurs at this potential. However, only one peak is observed in the CV. Unfortunately, the DCVA signal at 1200 nm was not recorded due to the limitation of the present hardware.

The results of the *in-situ* conductivity experiments, for a 1- μ m thick film during the growth are shown in Fig. 6. The current flowing through the interdigitated film increases as the applied potential increases from -0.6 to 0.8 V. Then the current remains at the same level until 1.6 V. In the presence of the 3-methylthiophene monomers, the current increases as the film grows.

Similar data have been collected for a film of 5 μ m thickness in 0.5, 0.05, and 0.005 M LiClO₄. Small increases in currents are observed as the concentration of the supporting electrolyte increases. Since conductivity is directly proportional to the current, the conductivity of the film increases from -0.6 V to 0.8 and is maintained from 0.8 to 1.8 V in the absence of monomer. However, in the presence of monomers, the conductivity increases at 1.6 V when electropolymerization occurs.

CONCLUSION

This report has demonstrated the utility of the DCVA and related techniques in studying P3MT. From the observations reported in this study, we can draw the following conclusions:

- (1) The oxidation of the P3MT film is controlled by diffusion of counter ions. This is illustrated by the shifts in DCVA peak signals in the anodic direction at 482 nm as the film thickness increases.
- (2) It has been shown by NNIRS visible spectra and DCVA measurements that what appears as a single CV peak consists of currents arising from more than one redox processes.
- (3) *In-situ* conductivity measurements indicate that the generation of bipolarons does not change the conductivity of the film. In polyaniline, the conductivity of the film decreases as the film becomes bipolaronic [16].

ACKNOWLEDGEMENT

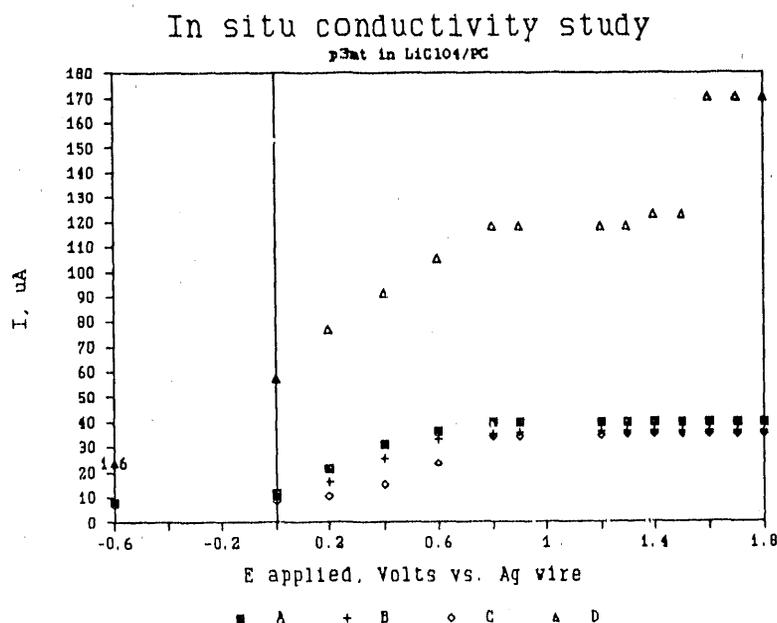


Fig. 6. Results of current vs. E applied of P3MT film: $5 \mu\text{m}$ in (A) 0.5, (B) 0.05 & (C) 0.005, M LiClO₄/PC; (D) $1 \mu\text{m}$ as in (A).

We wish to thank M. B. Sinclair and M. A. Valdez, Sandia National Laboratories, for the fabrication of the electrode for the conductivity experiment. This work was supported by the United States Department of Energy under Contract DEAC04-76DP00789.

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